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Exhaust Emission Patterns from Two Light-Duty Diesel Automobiles

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Research Triangle Park, NC

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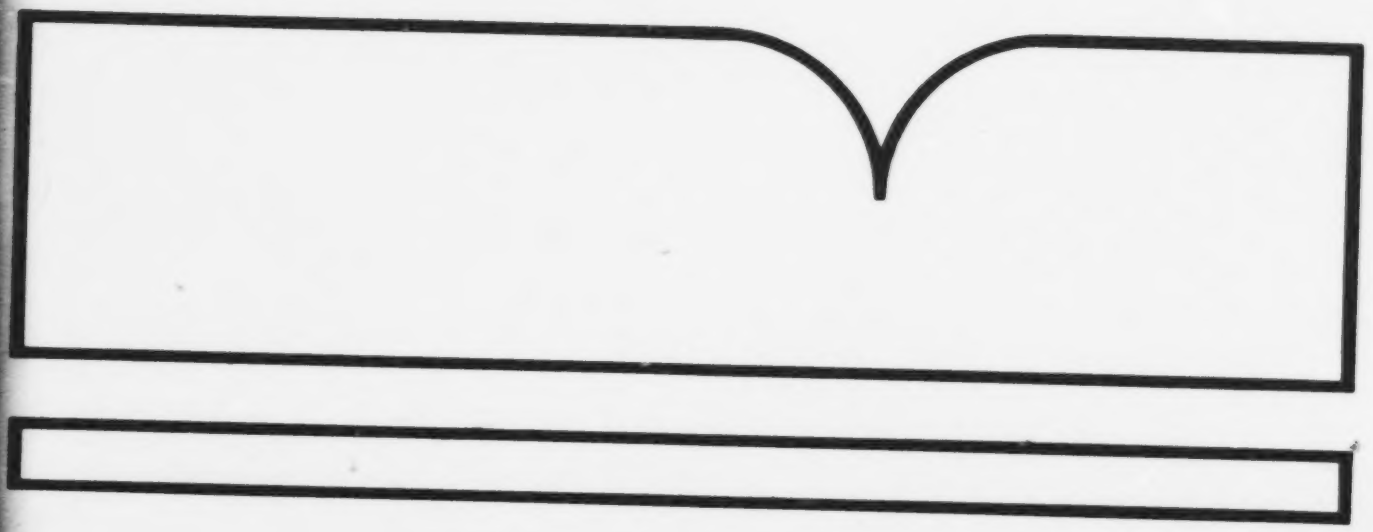

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16. ABSTRACT

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ABSTRACT

Particulate and gaseous emissions from two light-duty diesel automobiles were examined over six operating cycles. Particulate characterizations included mass emission rate, soluble organic content, and trace element content determinations. The particulate matter was sampled using both a total filtration system having 20 X 20 inch filters and a conventional probe arrangement employing 47 mm filters. Bioassay of selected diesel particulate extract was carried out using the Ames test procedure. Gaseous characterization included real-time analysis of regulated exhaust emissions. A special operating schedule was developed for each test car using the real time system to modally determine the effect of acceleration rate on regulated gaseous emissions.

INTRODUCTION

Exhaust emissions from light-duty diesel automobiles have been under investigation over the past several years. When the diesel engine became a candidate for high volume production in the United States, much of the work focused on the emission of regulated gaseous pollutants (1-5)* In addition to demonstrating itself as a fuel efficient engine possessing performance characteristics compatible for automotive use, the light-duty diesel became recognized for its low emission of regulated gaseous pollutants.

Later, as the diesel automobile increased in popularity, investigators began to examine diesel exhaust in greater detail. Efforts were undertaken by some to characterize both the unregulated gaseous and particulate fractions of light-duty diesel exhaust. (6,7,8) Because findings had shown particulate emission rates from diesels to be relatively high, most of the attention was directed at the character of these emissions.

Diesel exhaust particles predominate in size ranges less than 10 microns. They are generally composed of carbonaceous material with substantial quantities of extractable organics. These small particles are able to survive transport to lung tissue where deposition presumably occurs. Two serious concerns are the health consequences associated with deposition in the lung and the extent to which the organics participate in photochemical reactions within the atmosphere. Reflecting these concerns, a great deal of emphasis is currently being placed upon the further chemical characterization of diesel exhaust particles and the assessment of any significant health risks associated with the organic fraction.

The study reported in this paper investigates gaseous and particulate matter emissions trends from two diesel automobiles. Regulated gaseous emissions are examined utilizing a real-time analysis system recently developed at the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. Using this system, an effort is made to modally determine the effect of different acceleration rates upon exhaust emissions. Particulate matter emission rates are examined over six separate test cycles using two different collection techniques: the total diluted gas filtration method and the more conventional probe method. The characterizations of particulate matter show the quantitative presence of the soluble organic fraction (SOF), trace metals, and SOF molecular weight distributions. Bioassay test results obtained for a select portion of the particulate organic extractions are also presented.

VEHICLE AND FUEL DESCRIPTION

The two test vehicles used in this study are decribed in Table 1. The Rabbit diesel was purchased new by EPA and underwent a break-in period with mileage accumulation prior to testing. The Oldsmobile diesel was on loan to EPA from General Motors and had been operated on the test fuel for over 1000 miles before being tested.

* Numbers in parentheses designate references at end of paper.

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Table 1 - Description of Test Vehicles

	OLDSMOBILE DIESEL	VW RABBIT DIESEL
MODEL YEAR	1980	1980
VEHICLE SIZE	FULL-SIZE	SUBCOMPACT
NUMBER OF DOORS	4	2
NUMBER OF PASSENGERS	6	4
ODOMETER, mi.	11,500	1,500
NUMBER OF CYLINDERS	V-8	I-4
DISPLACEMENT, liters	5.7	1.5
COMPRESSION RATIO	23:1	23:1
OUTPUT POWER, HP	–	48
TRANSMISSION TYPE	AUTO	MANUAL
SPEEDS	3	4
INERTIA TEST WT., lb.	4500	2250
ROAD LOAD, HP AT 50 mph	11.4	6.8
EGR EQUIPPED	YES	NO
COMBUSTION CHAMBER	PRECHAMBER	PRECHAMBER

The diesel fuel which was used in this study was obtained through a local commercial vendor. Inspection results for the fuel are shown in Table 2. Aside from this fuel's rather high aromatic content, it resembles the National Average Number 2 diesel fuel. National Average fuel has a Cetane Number of 48.7, a sulfur content of 0.23 percent by weight, and an End Point of 638°F. The fuel used in this study has corresponding values of 46, 0.18 percent, and 638° F. Its aromatic content of 39.9 percent is somewhat higher than the 29.8 percent for the National Average.

FACILITY DESCRIPTION

This test program was conducted within a test cell which contains a chassis dynamometer for vehicle road load simulation. The dynamometer, manufactured by Burke Porter, simulated road load by means of a DC electric motor-generator directly coupled to the front rolls of the dynamometer. A Reliance analog control system was used to vary armature current to achieve the desired motor torque. The electric drive can add or subtract torque to produce simulated inertias from 1,500 to 5,500 pounds at 250 pound increments. The dynamometer rolls are 9.5 inches in diameter and the front rolls were chain coupled to the dynamometer's rear rolls. The roll coupling feature was added to reduce the vehicles' tendency to rock within the rolls during heavy acceleration and deceleration.

Exhaust gases from the test vehicle were directed via a 3 in diameter flexible stainless steel line to an 8 in diameter dilution tunnel (Figure 1). Within the dilution tunnel raw exhaust gas was thoroughly mixed with filtered diluent and the diluted mixture drawn through the system by two positive displacement pumps located downstream. These pumps operated either separately or in parallel when maximum flow was desired. Flowrates through this constant volume system (CVS) were capable of being varied from about 170 standard cubic feet per minute (SCFM) to about 1200 SCFM, thus making it possible to vary dilution ratios within the tunnel. This capability was desirable as a means of controlling temperature within the tunnel to levels required for sampling particulate matter. It also permitted some control over species concentrations within the sampling system. For example, control over the level of nitrogen dioxide (NO_2) in the diluted gas stream was essential in order to reduce the effect of nitrated artifacts on bioassay test results.

Table 2 - Description of Test Fuel

SOURCE	AMOCO
TYPE	2-D
GRAVITY, API	33.9
DENSITY, g/ml.	0.8551
SULFUR CONTENT, wt. %	0.18
CETANE NUMBER	46.0
DISTILLATION TEMP., °F	
IBP	357
10%	428
50%	509
90%	597
EP	638
FIA, %	
AROMATICS	39.9
OLEFINS	2.0
SATURATES	58.1

TEST SEQUENCE AND CYCLE DESCRIPTION

RUN SCHEDULE-Both the Rabbit and Oldsmobile diesels were tested in similar test plans which were designed to obtain particulate samples over six different cycles and gaseous modal data from three cycles. The six cycles were the 1975 Federal Test Procedure (75 FTP), the Highway Fuel Economy Test (HFET), the Congested Urban Expressway Cycle (CUE), the New York City Cycle (NYCC), the Special Cycle (SC), and a 10 minute 45 mph steady state test (45 SS). The test sequence and sampling effort is summarized in Table 3. Except for the FTP's, each test cycle followed the previous test cycle by a fifteen minute hot soak period.

Real-time gas analysis was performed over the 1975 Federal Test Procedure (FTP), the "unclipped" Federal Test Procedure (FTP-U), and the Special Cycle (SC). The Special Cycle is a 24-mode cycle developed within the program to evaluate the effects of different acceleration rates on regulated gaseous emissions. The "unclipped" FTP was conducted like the 1975 FTP except that the original speed-time trace was used (9). This original trace was modified by reducing a few of the heavy accelerations to obtain the FTP version which is currently the standardized speed-time trace (10). For example, the FTP-U contained a maximum

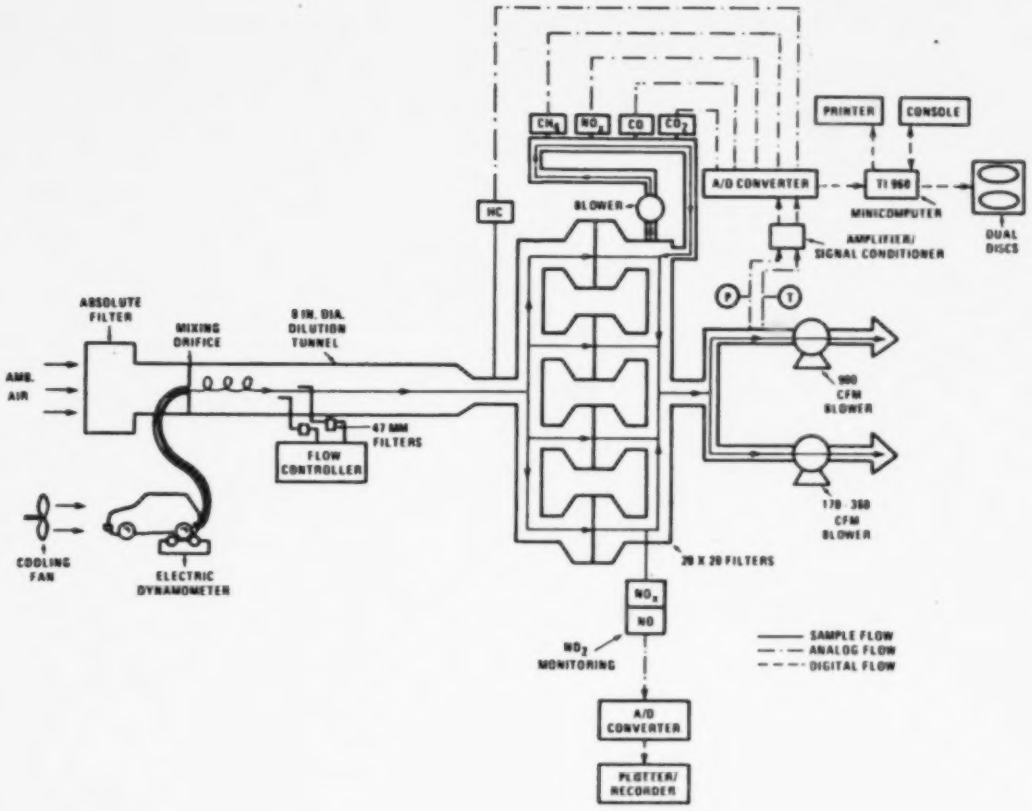

Fig. 1 - The sampling scheme

Table 3 - Test Sequence and Sampling Effort

	DATA ACQUISITION EFFORT*	ACTIVITY
DAY 1		PREP VEHICLE
DAY 2	A, B, C, D, E	FTP
	B, C, D, E	HFET
	B, C, D, E	CUE
	B, C, D, E	NYCC
	B, C, D, E	SC
	B, C, D, E	45 mph S.S.
DAY 3	A, C, E	FTP
	A, C, E	SC
	A, C, E	SC
DAY 4	A, C, E	FTP (u)
	A, C, E	SC
	A, C, E	SC
DAY 5	A, C, E	FTP (u)
	A, C, E	SC
	A, C, E	SC

*KEY: A - REAL TIME GAS ANALYSIS
B - 47 mm FILTERS
C - 20 in. x 20 in. FILTERS
D - NO_2 MONITOR
E - BAG GAS ANALYSIS AND FUEL ECONOMY

acceleration of 5.6 mph per second while the FTP contained no acceleration in excess of 3.3 mph per second. This "clipping" of acceleration rates was effected to avoid operating in excess of specification limits for early dynamometers.

SPECIAL CYCLE DESCRIPTION AND DEVELOPMENT-In order to better evaluate the effect of varying acceleration rates upon exhaust gas emissions, a Special Cycle was devised. The cycle contains 24 distinct modes including two accelerations at wide open throttle (WOT), two at 85 percent of the WOT rate, and two at 70 percent of the WOT rate. The decelerations were made equal but opposite to the accelerations which immediately preceded them. A speed-time trace for the Special Cycle is shown in Figure 2. The idle and 50 mph cruise modes extended for a long enough period to insure time for the gas analyzers to settle out. The total distances covered were 6.9 miles for the VW cycle and 7.3 miles for the Oldsmobile cycle. Different cycles were required for each car since their WOT acceleration rates were different.

Because all acceleration and deceleration modes within the cycle were derived from the WOT acceleration rate, WOT accelera-

tion curves were needed for each car. They were obtained by accelerating at WOT in both directions over a level section of road on a day when wind speeds were negligible. The cars were equipped with a fifth wheel and strip chart recorder for data collection. From these data an average WOT acceleration curve was plotted and the associated 85 percent and 70 percent curves were drawn using a Hewlett Packard 9100 series plotter and calculator unit. The 85 and 70 percent WOT curves represent, respectively, curves having a slope at each given speed value equal to 85 and 70 percent of the slope obtained at WOT.

The WOT data were generated in an actual road test because the dynamometer was not available at the time. As it happened, the speed-time trace recorded at WOT on the road agreed well with that recorded on the dynamometer, thus demonstrating that the road and inertia loads were being properly simulated by the dynamometer.

GASEOUS EMISSION MEASUREMENT EQUIPMENT AND PROCEDURES -Regulated gaseous emissions, CO_2, and methane (CH_4) were determined using standard bag sampling and analysis procedures in accordance with the Federal Register (11). In numerous test runs, these same emissions were measured to obtain modal emissions data using a real-time system centered around a TI-960 B minicomputer.

When the real-time system was in operation, diluted exhaust gases were branched off from the CVS system through a 1 in diameter line. A small blower located within this line transported the gases to the vicinity of the exhaust gas analyzers. This arrangement reduced delay times associated in moving the sample from the main CVS line to the analyzers.

Analog outputs from the gas analyzers were directed to the computer through analog to digital A/D converters (see Figure 1). In addition to gas data, temperature and pressure levels at the inlet to the CVS and air flowrates into the diesel engine were also monitored continuously. These inputs to the computer made possible the modal calculation of CVS flowrates corrected to standard atmospheric conditions and diluent to raw exhaust (dilution ratio) ratios within the CVS - tunnel system.

The A/D converter system used a programmable gain amplifier to provide 13 full scale input signal ranges from 2.5 mv to 10.24 v. It converted the analog signals to 13-bit binary numbers. Although the converter was configured with forty input channels, only sixteen were programmed for use. Each channel was sampled at a rate of ten samples per s.

The digital data outputted from the A/D converter was stored in one of two memory buffers of the computer. The two buffers alternately filled and dumped their contents onto a disc unit. Thus, the data was gathered continuously and stored serially within a large disc file during test runs.

At the completion of a run, a program was loaded and information was retrieved from the disc for processing. The data retrieval and processing program basically integrated all data points within the defined modes and calculated average diluted exhaust concentrations, dilution ratios, and CVS flowrates. It also calculated the modal emission rate in grams per mile for hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_x), CO_2, and CH_4. The mode definitions were made at the beginning of the program by inputting mode type, time, and distance information which were stored on cassette tape. Because all gas data generated during the test remained stored on the disc, the same run could be evaluated using different modal analysis schemes. It was also possible to concentrate on certain portions of the cycle not presently defined within the modal scheme.

When utilizing the real-time system during the 1975 FTP and the FTP-U cycles, a modal scheme developed at General Motors was used. A breakdown showing the modes and their duration is shown graphically with the FTP speed-time trace in Figure 3. Data on regulated emissions, CO_2, and CH_4 was integrated by mode such that average emission rates for each mode were calculated. The

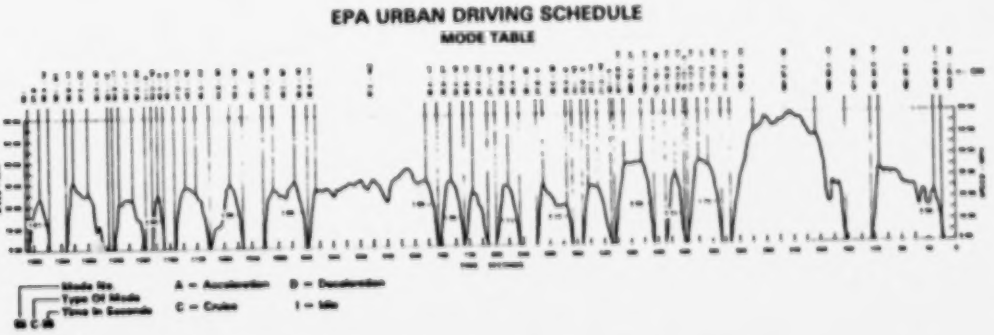

Fig. 2 - Special cycle for Oldsmobile Diesel

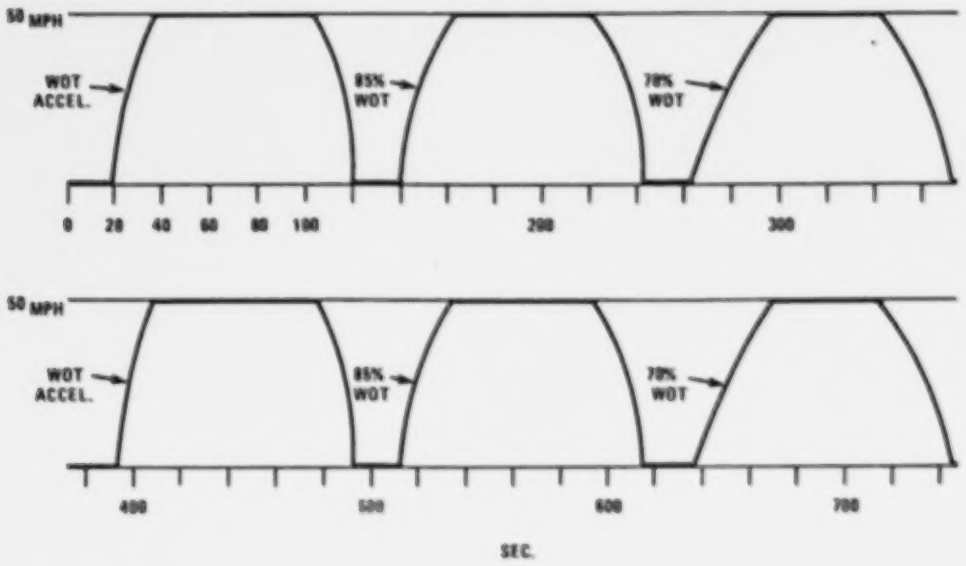

Fig. 3 - FTP mode table

processed data also calculated the emission rates for each of the three phases of the FTP.

PARTICULATE ANALYSIS AND MEASUREMENT EQUIPMENT AND PROCEDURES

PARTICULATE SAMPLING STATIONS-Particulate matter in diluted exhaust was sampled using both a conventional method employing twin probes with 47mm filters and a total diluted gas filtration system employing four rather massive 20 inch by 20 inch filters in parallel. Both sampling methods were operated concurrently during test runs.

Sample flowrates through the probe filters were kept constant with a flow controller, a method that involved varying a flow regulator downstream to maintain a constant pressure drop acrossed a flow orifice. Each probe contained a primary and back-up filter and sampling of particulate matter was done in accordance with the EPA Standard for Emission of Particulate Regulation of Diesel-Fueled Light-Duty Vehicles and Light Duty Trucks (12). Because of the twin probe arrangement, duplicate filters were collected whenever possible during tests.

The 20-in by 20-in filters were used to collect large quantities of diesel particulate matter for extract to be used in Ames testing. The filters were configured and sized to permit sampling of the total diluted exhaust gas stream. With these methods, all the exhaust particles generated by the vehicle during testing were captured.

Particles sampled for particulate emission rate determination and for work involving the extraction of organic material were collected on Pallflex T60A20 teflon-coated glass fiber filters. The Pallflex filter was selected because the fibers do not appear to interact with gaseous organics and the pressure drop across the filter does not become excessively high during collection (13). Particles destined for x-ray analysis in trace metal determination were collected on Fluoropore filters, which have been found to be well suited for this procedure.

47MM FILTER HANDLING - Prior to testing, the filters were weighed and placed within filter holders which were situated in-line on the sample probes (see Figure 1). Sample flowrates were maintained at about 1 SCFM with teflon-coated glass fiber filters and at about 0.6 SCFM with the Fluoropore filters. Following the test, the filters were removed, inserted in petri dishes, and transported to a temperature and humidity controlled weighing room for equilibration. Sample weight was later recorded and the gram per mile emission rate was calculated. For the FTP, a "weighted" emission rate was calculated by breaking out the emission rates for each of the three test phases and applying weighting factors. This procedure was made possible by the fact that a separate filter had been collected for each test phase.

After the sample weights had been determined, the teflon-coated glass fiber filters were placed within separate soxhlets for extraction of organic materials. The extraction process was carried out for 8 h using methylene chloride as the solvent. The amount of organic extract present was determined by two methods: the direct method and the Delta Filter Method.

The direct method involved three stages. Initially the filters were placed within the soxhlets for extraction of the organics, as explained earlier. The extracted solution was "blown down" under vacuum at a temperature of about 30°C removing much of the highly volitile solvent. The highly concentrated

solution was then transferred to vials (that had been weighed prior to the extraction process) and dried rapidly by bathing in gaseous nitrogen. After equilibrating in the weighing room, the vials were reweighed and the precent extractable derived by taking the difference of the two weights.

The second method, the Delta Filter Method, was considerably shorter requiring only the initial extraction stage. After the filters had been extracted for 8 h they were removed from the soxhlets and placed into petri dishes. Then the filters were vacuum dried 1 h in an oven at a temperature of about 85°C. After drying, the filters were removed to the weighing room and allowed to equilibrate overnight. The next day the filters were reweighed and a new sample weight was recorded. The percent extractable was derived by subtracting the sample weight after extraction from the sample weight before extraction.

X-ray analysis was carried out on the Fluoropore filters to determine the quantity of various trace elements in the particulate matter. The instrumentation used for these analyses was a Siemens MRS-3 x-ray fluorescence spectrometer. It is automated and computer-controlled, with 16 fixed monochromators and one scanning monochromator. Counting intervals are normally 100 s for the fixed monochromators and 20 s for the scanning monochromator.

20-IN x 20-IN FILTER HANDLING - The large 20-in square teflon-coated glass fiber filters were used in groups of four (one per filter holder) per test. Except for those gas streams sampled by the 47 mm filters, the 20 x 20's sampled the entire diluted exhaust gas stream. The filters were weighed in groups of four both before and after the test. The particulate emission rate was easily calculated as the sample weight on the filters divided by the test cycle distance. Emission rates so calculated were later compared with those calculated from 47 mm filter data.

Large quantities of extracted material necessary for Ames testing were obtained from the large 20-in x 20-in filter samples collected during each test. These were immediately weighed and stored at -20°C, prior to preparation of organic extracts of exhaust particulates for Ames testing and chemical characterization. Typically, two 20-in x 20-in filters were soxhlet extracted with methylene chloride overnight and the extract filtered through a 0.2 um Millipore filter. The solvent was then reduced to 100 ML on a rotary evaporator, and a 2 ML aliquot evaporated under nitrogen to determine the extracted mass. A larger aliquot for the Ames bioassay was similarly prepared.

BIOLOGICAL TESTING-Ames testing of extracts was conducted by Northrop Services, Inc., RTP, N.C. Samples were tested in strain TA 98 of the Ames Salmonella typhimurium mutagenisis bioassay. (14) The extract samples, which were supplied dried and under nitrogen, were diluted to 2 mg per ml in dimethyl-sulfoxide and assayed at doses of 50, 100, 300, and 500 ul. Specific activities were calculated from the linear portion of the dose response curve, which in all samples was limited to the spontaneous revertant level plus the 50 and 100 ul doses. All samples were tested in a single experiment.

MONITORING NO_2-An NO_2 monitor was operated on days when the complete six cycle sequence was run (i.e., day 2 of Table 3). It was operated only as necessary to define the average and peak levels of NO_2 in the diluted exhaust sample. This action was taken to document NO_2 levels because potential for interaction between NO_2 and poly-nuclear aromatic compounds to yield nitro species which are direct mutagens in the Ames bioassay procedure has been reported (15). Furthermore, NO_2 emissions from diesel engines have been reported as representing at times a significant fraction of the overall NO_x emissions (16). Forthcoming purblications from this laboratory will address more directly the nitrate artifact problem relative to diesel engine exhaust sampling.

The levels in diluted exhaust gas were monitored continuously by recording the difference between outputs from a NO_x analyzer and an NO analyzer. Both analyzers were identical TECO chemiluminescent types, except that the NO analyzer was operated without a converter. The response time of each analyzer to a pulse of NO injected into the dilution tunnel was equated by adjusting sample line lengths to the analyzers. This precaution insured that the analyzers detected the same sample when the difference measurement was taken.

Analog outputs from each analyzer were inputted into a Bascom Turner Model 8110 analog to digital recorder/plotter. Data was digitized, loaded into a buffer, dumped onto a floppy disc, and later retrieved for plotting and integrating. The recorder automatically calculated the difference measurement, plotted the NO_2 level versus time, and integrated to obtain the average level over the cycle.

GASEOUS EMISSION RESULTS

CONSTANT VOLUME SAMPLING SYSTEM-The regulated gaseous emissions and fuel economy data were obtained routinely by the conventicnal CVS procedure described earlier. The results (Table 4) represent the mean levels determined for the two diesel cars. The number of tests conducted to arrive at the mean and the standard deviations are also reported. Emissions data obtained for the Rabbit diesel during a period when fuel injector problems existed have not been averaged into the data reported in Table 4.

Regulated emissions from the Oldsmobile diesel are below the 1980 emission standards level, while hydrocarbon emissions from the Rabbit diesel are somewhat higher than the 0.4 g/mi level. As mentioned earlier, the Rabbit diesel had been purchased only a month before

Table 4 - Comparison of 75 FTP, FTP-U, HFET, CUE, NYCC, SC, and 45 mph SS Gaseous Emissions Data, g/mi

VEHICLE/TEST		HC	CO	NO_x	CH_4	FUEL ECONOMY, mpg	NO. OF TESTS
OLDSMOBILE DIESEL							
75 FTP	C	0.255	1.244	1.541	0.001	19.671	7
	σ	0.035	0.172	0.195	0.002	1.281	
FTP-u	C	0.281	1.390	1.601	0.001	16.956	3
	σ	0.033	0.099	0.111	0.000	0.040	
HFET	C	0.139	0.846	1.014	–	27.101	3
	σ	0.020	0.030	0.085	–	1.276	
CUE	C	0.171	1.048	1.096	0.002	26.466	3
	σ	0.034	0.084	0.171	0.001	3.398	
NYCC	C	0.734	3.195	2.583	0.001	9.430	3
	σ	0.135	0.386	0.312	0.023	0.388	
SC	C	0.193	1.501	1.179	0.005	22.290	10
	σ	0.031	0.165	0.081	0.003	0.700	
45 mph, ss	C	0.091	0.444	1.114	–	34.961	3
	σ	0.010	0.021	0.147	–	1.241	
VW RABBIT DIESEL							
75 FTP	C	0.505	1.311	0.989	0.027	30.383	4
	σ	0.042	0.019	0.076	0.014	1.569	
FTP-u	C	0.447	1.603	1.130	0.033	37.307	3
	σ	0.027	0.359	0.291	0.010	4.569	
HFET	C	0.532	1.210	1.030	0.049	40.805	3
	σ	0.068	0.092	0.044	0.024	0.436	
CUE	C	0.613	1.260	1.011	0.008	42.841	3
	σ	0.054	0.154	0.118	0.020	2.396	
NYCC	C	1.026	2.507	1.703	0.013	26.048	3
	σ	0.078	0.066	0.226	0.004	1.262	
SC	C	0.506	1.360	0.883	0.036	42.779	6
	σ	0.027	0.105	0.120	0.009	0.861	
45 mph, ss	C	0.268	0.839	0.932	0.013	50.829	3
	σ	0.019	0.062	0.122	0.000	1.393	

the test program began and initial emissions results indicated an engine malfunction condition (see Table 5). The car was returned to the dealer for examination of the injector spray patterns and engine timing. After determining that the injector timing had been somewhat retarded, it was advanced three degrees and the test program was resumed. As the results in Vehicle Condition "B" of Table 5 demonstrate, emissions generally deteriorated after the timing was advanced. For this reason, the vehicle was returned to the dealer for recheck of the injector spray patterns. This time one of the injector tips was defective and it was replaced. A subsequent reduction (condition "C," Table 5) in both gaseous and particulate emissions was noted, although the HC and CO values were still significantly higher than values obtained by EPA in certification.

Table 5 - Emission Trends from Rabbit Diesel

VEHICLE* CONDITION	TYPE TEST	HC, gm/mi	CO, gm/mi	NO_x, gm/mi	PARTICULATE, gm/mi	FUEL ECONOMY, mpg
A	FTP	0.88	1.68	1.23	0.94	29.0
B	FTP	0.34	1.70	1.26	0.76	26.5
C	FTP	0.51	1.31	0.99	0.43	29.4
CERT	FTP	0.38	1.16	1.05	*	40.2
A	SC	0.73	2.01	0.96	0.60	43.1
B	SC	0.90	1.66	0.88	0.55	39.0
C	SC	0.51	1.36	0.89	0.48	42.8

*A - TIMING RETARDED/BAD INJECTOR
B - BAD INJECTOR
C - INJECTOR TIP REPLACED
CERT - CERTIFICATION RESULTS FOR 1980 DIESEL RABBIT
* - NOT AVAILABLE

Concern that the new engine was not broken in properly and that blow-by emissions might exist prompted an examination of the SOF molecular weight distributions. This examination identified the principle sources of the organic mass by use of a gas chromatograph, which Black and High have reported to be a useful tool in detecting lubricant consumption (13). The distributions were examined to insure that the engine had been broken-in from an emission standpoint. Figure 4 shows the distribution for the Rabbit. This molecular weight distribution curve and the one shown in Figure 5 for the Oldsmobile represent the average distributions obtained over the six test cycles examined. The lack of abnormally high quantities of the lube oil components (C-25 to C-40) implies that lube oil consumption was not a problem for either vehicle. For the Rabbit, however, high levels of the fuel component were evident out to about C-25, suggesting that a fuel delivery problem continued to exist. The somewhat elevated HC and CO emissions from the Rabbit diesel were attributed to this problem.

REAL-TIME SAMPLING AND ANALYSIS - Regulated gaseous emissions were determined modally over the 75 FTP, FTP-U, and the SC tests using the real-time sampling system described earlier. Table 6 presents the percentage difference in emissions determined by using the CVS procedure versus the real-time system. In general there appears to be good agreement between the two methods. Table 7 shows the comparison between standard deviations (standard deviations are expressed as a percent of the mean) obtained when using the CVS procedure and the real-time system. The repeatability of the real-time system was even better in most cases than the CVS procedure, which was in itself satisfactory. Because air flowrate into the diesel engine was monitored on a continuous basis with the real-time system, modal determination of the actual dilution ratios within the CVS was possible. The average dilution ratio over each test cycle or test phase could also be determined; hence, correction for background emissions which includes this dilution ratio value could be calculated more directly. Because the calculation of dilution ratio in accordance with the Federal Register procedure (11) assumes stoichiometric combustion, which for diesels is an unrealistic assumption, it was of interest to compare results obtained using the Federal Register procedure with those obtained using the direct measurement method. The results in Table 8 are the same for all practical purposes. The percent difference only becomes significant when the emissions level becomes very low. For example, the HC emission rate for Phase 2

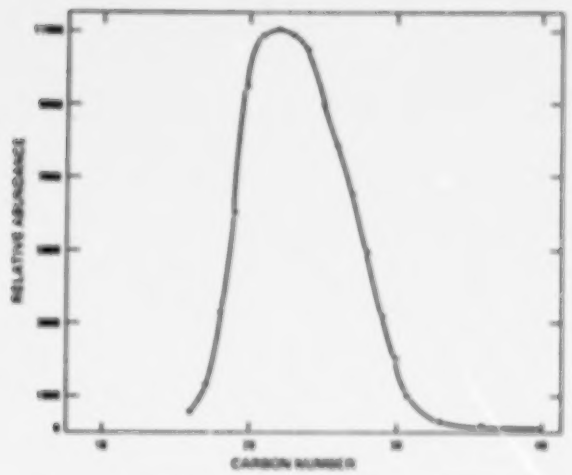

Fig. 4 - Molecular weight distribution for particulate SOF - VW Rabbit

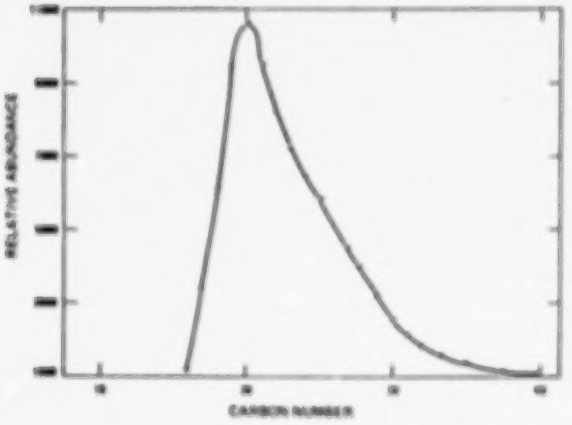

Fig. 5 - Molecular weight distribution for particulate SOF - Oldsmobile

was 0.25 g per mi with the calculated dilution ratio versus 0.27 g per mi with the measured ratio, a difference of about 8 percent. The calculated and measured dilution ratio values are also shown in Table 8 for each of the three phases of the FTP.

The modal analysis system made it possible to determine the effect of differing acceleration rates upon gaseous emission patterns and to examine the difference in emissions between the FTP and the FTP-U. Because the FTP-U contained a few higher accelerations than the FTP, some knowledge of the emission rate differences between the two cycles was desired.

While the gaseous data presented in Table 4 for the Oldsmobile do support expectations for an increase in emissions and fuel consumption over the FTP-U test cycle, the data for the Rabbit diesel do not. To better

Table 6 - Percentage Difference in Emissions Determinations - CVS Procedure vs. Real-Time.

VEHICLE/TEST	Δ HC, percent	Δ CO, percent	Δ NO_x, percent
OLDSMOBILE DIESEL			
75 FTP	+ 2.4	- 5.5	- 2.8
FTP-u	+ 2.5	- 7.9	- 6.7
SC	+ 3.7	- 8.6	- 1.3
VW RABBIT DIESEL			
75 FTP	+ 6.4	- 5.7	+ 0.5
FTP-u	+ 3.8	+ 10.1	+ 6.1
SC	+ 5.2	- 1.4	+ 3.7

Table 7 - Comparison of Test-to-Test Repeatability* for Oldsmobile - CVS Procedure vs. Real-Time

TEST/METHOD	HC	CO	NO_x	CO_2
75 FTP				
CVS	14	14	12	6
REAL TIME	8	8	14	5
FTP-u				
CVS	11	7	7	2
REAL TIME	13	1	2	3
SC				
CVS	10	11	7	3
REAL TIME	10	12	4	1

*REPEATABILITY EXPRESSED AS THE PERCENT OF THE STANDARD DEVIATION OF THE MEAN: [STANDARD DEVIATION/MEAN] X 100

Table 8 - Comparison of Oldsmobile FTP Data Obtained with Calculated Versus Measured Dilution Ratio

TEST PHASE/METHOD	CO_2, g/mi	HC, g/mi	CO, g/mi	NO_x, g/mi	DILUTION RATIO
NO. 1					
CALCULATED	615.31	0.44	1.85	1.35	8.99
MEASURED	616.72	0.46	1.86	1.35	8.23
NO. 2					
CALCULATED	628.83	0.25	1.34	1.87	12.64
MEASURED	630.08	0.27	1.35	1.85	5.68
NO. 3					
CALCULATED	595.60	0.29	1.47	1.48	8.10
MEASURED	594.97	0.25	1.48	1.49	8.05

understand what was happening, it was necessary to examine the modal data.

Mode 6 of the FTP-U contained the highest acceleration rate encountered throughout the test. The rate from 0 to 15 mph had a value of 4.7 mph per s as compared with a value of 3.3 mph per s for the FTP. Ten s following the start of the acceleration, the speeds leveled off to an approximate value of 28 mph in both cycles.

A look at the Rabbit modal data revealed no substantial differences in emissions between the FTP and FTP-U versions of Mode 6. A closer examination of the WOT acceleration rate for the Rabbit indicated that the rate from 0 to 15 mph was 3.7 mph per s. This meant that the vehicle was being operated at a near WOT acceleration rate in the FTP and that at WOT in the FTP-U, the vehicle was unable to keep up with the trace. Thus, emission trends resulting from differing acceleration rates could not be successfully understood by comparing FTP data with FTP-U data when the vehicle was unable to accelerate at rates required by the cycle. (Although more gradual accelerations existed in both cycles, those were of less impact.)

When emissions from the Oldsmobile were examined s by s over the first 10 s of Mode 6, the difference between FTP and FTP-U emissions of CO, HC, NOx, and CO_2 were, respectively, 6, 4, 2, and 1 percent. While the emissions differences cited in Table 4 do not appear significant, the difference in fuel economy does. From the data collected within this program, the reason for this marked difference is not apparent.

The effect of varying acceleration rates upon exhaust emissions was examined with greater focus over the Special Cycle (SC) test runs. The SC, which was described earlier, contained accelerations at WOT, 85 percent of WOT, and 70 percent of WOT. Figures 6 and 7 show emissions trends observed from the Rabbit and Oldsmobile diesels.

CO emissions from the Rabbit show the greatest sensitivity to increases in the acceleration rate, while NOx emissions appear almost insensitive to changes. CO emission increased about 60 percent when going from the 70 percent rate to WOT. HC emissions showed virtually no increase when the acceleration rate rose from 70 to 85 percent of WOT; however, the increase from the 85 percent rate to WOT affected a 54 percent increase in emissions. CO_2 emissions, which reflect the vehicle's fuel consumption rate, increased by about 5.5 percent when testing at the 85 percent rate, as opposed to the 70 percent rate. Another increase of 22 percent was noted when going from the 85 percent rate to the WOT rate.

The emission trends observed from the Oldsmobile were more sensitive to increases in the acceleration rate. Emissions of HC, CO, and NO_x increased 128, 52, and 39 percent, respectively, as the acceleration rate was increased from the 70 percent rate to the WOT rate. CO_2 emissions exhibited a rather steady increase of 43 percent as the acceleration rate was increased over the range.

It should be remembered that the emissions in Figures 6 and 7 are expressed on a g per mi basis. Because the vehicle was accelerated at different rates to a cruise speed of 50 mph, the distances and times over the differing accelerations varied. This resulted in portrayals which made the emissions at higher accelerations appear somewhat exaggerated. For

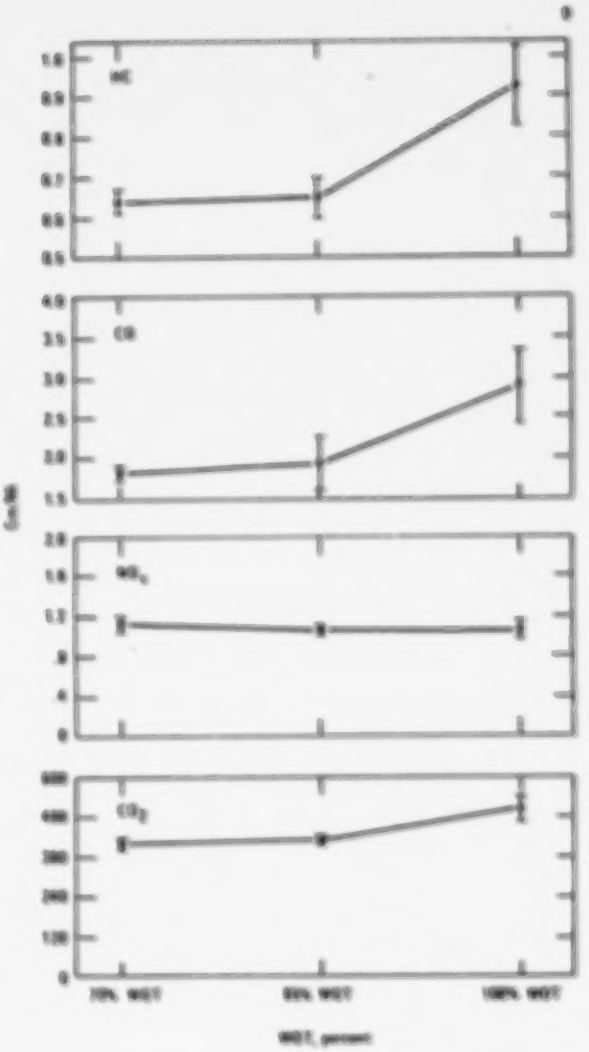

Fig. 6 - VW Rabbit emission trends with change of acceleration rate

example, the mass emission of HC from the Rabbit over a 1 mi course was 0.582 g when the vehicle was accelerated at WOT then operated at a 50 mph cruising speed. The mass emission was reduced to 0.495 g when the acceleration was lowered to 70 percent WOT and the remainder of the 1 mi course was driven at 50 mph. But this 15 percent reduction in mass emission appears small compared to the 54 percent reduction cited as the change in emission rate.

PARTICULATE MATTER EMISSIONS RESULTS

PARTICULATE MATTER EMISSION RATES - The emission rate of particulate matter from the test vehicles was principally determined by the sample probe method of collecting material on 47 mm filters. Because large 20-in by 20-in square filters were collected concurrently, emission rate determinations were worked up

from these as well. Table 9 shows the results with the means and standard deviations listed for each car.

The average of standard deviations within the sampling method using 47 mm filters was 11 percent and that within the 20 by 20 method was 17 percent. Considering this, agreement between the two sampling methods was good with the average difference equal to 14 percent. Emission rates were highest for each vehicle when tested on the New York City Cycle (NYCC). The NYCC has a duration of about 10 min, a distance of 1.13 mi, and an average speed of 7.1 mph. Hence, because of the low average speed of the cycle coupled with its "stop and go" nature, high emission rate values would be expected when expressed in units of g per mi. Emission rates from both vehicles appeared relatively insensitive to test cycle. The average emission rate from the Oldsmobile over all six test cycles was 0.54 g per mi with a standard deviation of 0.09 g per mi. For the Rabbit the average was 0.51 g per mi with a standard deviation of 0.11 g per mi. In both cases the standard deviations obtained from cycle to cycle are only slightly higher than the standard deviations obtained when testing within the same cycle.

Table 9 - Particulate Emission Rates

VEHICLE/TEST		SAMPLING METHOD: PROBE SAMPLING, gm/mi	SAMPLING METHOD: 20" X 20" SAMPLING, gm/mi
OLDSMOBILE DIESEL			
75 FTP	$\bar{x}$	0.54	0.54
	s	0.15	0.11
HFET	$\bar{x}$	0.58	0.46
	s	0.09	0.15
CUE	$\bar{x}$	0.53	0.41
	s	0.09	0.08
NYCC	$\bar{x}$	0.68	0.65
	s	0.05	0.07
SC	$\bar{x}$	0.53	0.44
	s	0.05	0.07
45 mi	$\bar{x}$	0.39	0.41
	s	0.04	0.07
VW RABBIT DIESEL			
75 FTP	$\bar{x}$	0.43	0.45
	s	0.03	0.05
HFET	$\bar{x}$	0.54	0.37
	s	0.11	0.21
CUE	$\bar{x}$	0.61	0.36
	s	0.03	0.03
NYCC	$\bar{x}$	0.64	0.66
	s	0.04	0.00
SC	$\bar{x}$	0.48	0.43
	s	0.01	0.01
45 mi	$\bar{x}$	0.35	0.36
	s	0.03	0.03

Table 10 - Soluble Organic Fraction of Particulate Matter

VEHICLE/TEST		% EXTRACTED BY DIRECT WEIGHING	% EXTRACTED "DELTA FILTER" METHOD	% DIFFERENCE BETWEEN METHODS
OLDSMOBILE DIESEL				
75 FTP	$\bar{x}$	15.20	15.22	3.30
	s	4.04	3.85	
HFET	$\bar{x}$	15.96	16.12	4.51
	s	2.46	2.39	
CUE	$\bar{x}$	14.35	14.60	6.13
	s	1.54	1.71	
NYCC	$\bar{x}$	15.05	14.75	6.05
	s	0.81	1.56	
SC	$\bar{x}$	11.07	11.39	6.59
	s	1.72	2.42	
45 mi	$\bar{x}$	28.94	28.87	3.25
	s	2.24	2.04	
VOLKSWAGEN DIESEL				
75 FTP	$\bar{x}$	27.13	26.22	5.46
	s	6.09	6.20	
HFET	$\bar{x}$	27.36	26.75	2.89
	s	5.24	5.53	
CUE	$\bar{x}$	29.63	29.03	3.01
	s	4.70	4.42	
NYCC	$\bar{x}$	26.79	24.16	13.79
	s	2.32	2.61	
SC	$\bar{x}$	27.69	27.31	4.89
	s	3.71	2.90	
45 mi	$\bar{x}$	31.93	31.92	4.30
	s	3.26	3.14	

SOF CONTENT - Table 10 shows the extractable organic as a percent of the total particulate matter from which it was extracted. Each vehicle registered its highest SOF's in the 45 mph steady state tests; however, levels from the Oldsmobile were significantly lower than the Rabbit's. Again the Rabbit's emission levels were relatively insensitive to the cycle while those from the Oldsmobile were significantly higher for the 45 mph steady state and lower for the Special Cycle.

As mentioned previously, the SOF content was determined by two different methods: the direct method and the Delta filter method. The direct method essentially weighs the extract directly while the Delta filter method takes the difference of the filter weight before and after extraction. Agreement between the two methods has been previously cited as being quite good (17). Although the samples obtained on 47 mm filters were considerably lighter in this study (the average sample weight equalling 8.3 mg), agreement between the two methods was within 8 percent for all filters examined. The difference expressed as a percent of the sample weight for all test cycle and vehicle combinations examined is given in Table 10. High difference values cited for the Rabbit when tested on the NYCC are mostly due to the extremely small sample quantities obtained over that cycle. The average sample weight for these tests was about 1.5 mg compared with an average of 13 mg for the HFET. Considering the small sample quantities involved, agreement is very good overall. Because great care must be taken to insure that the extract is properly dried before weighing in the direct method, the Delta filter method is somewhat easier to perform.

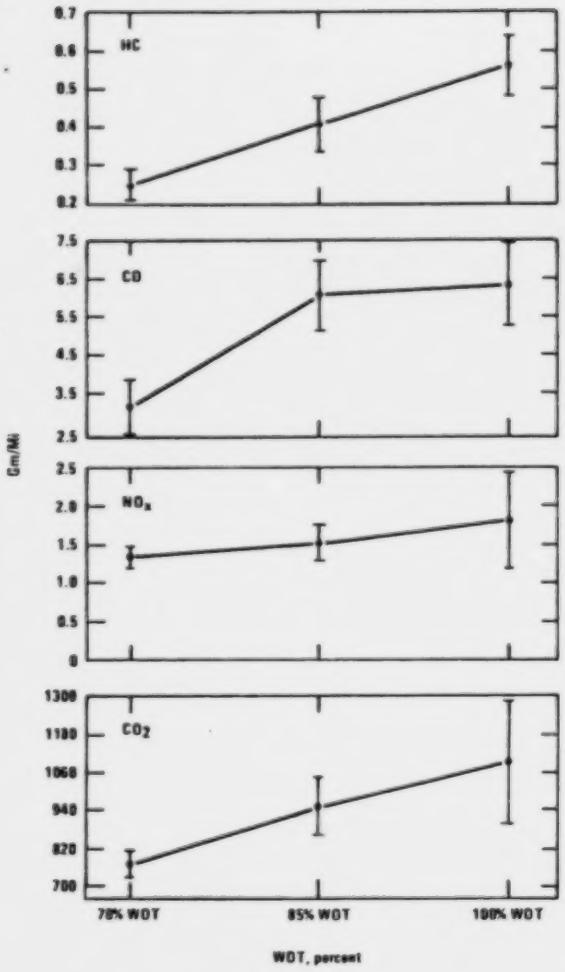

Fig. 7 - Oldsmobile emission trends with change of acceleration rate

TRACE METALS EMISSIONS - Tables 11 and 12 show the emission of trace metals or elements contained within the particulate matter. The predominant elements emitted from both cars were Na, Fe, Ca, S, Zn, and Sb. Of these, Na, P, Ca, and Zn are probably associated with the lubricating oil and its additives. Although the SOF molecular weight distributions (Figures 4 and 5) suggest that excessive oil consumption was not a problem, the x-ray data implies that lube oil consumption did exist to some extent. Fe emissions likely originated from exhaust system deterioration and S emissions from the fuel sulfur. Assuming that the particulate sulfur was contained as sulfate material ($=SO_4$), the sulfate represents 1.8 percent and 1.4 percent by mass of the total particulate emitted from the Oldsmobile and VW Rabbit, respectively. These percentages were fairly consistent regardless of test cycle since the relative standard deviations of the results were 21 percent for the Oldsmobile and 17 percent for the Rabbit over all six cycles. The weight percent sulfur content of the fuel was 0.18 which is close to the 0.23 National Average value.

For the FTP, the total elemental weight percentages of the total particulate matter emission from the Rabbit and Oldsmobile were 1.8 percent and 2.0 percent, respectively. These values agree closely with those cited by Hare and Baines (18) in their examination of emissions from two diesel automobiles. In that study, the total elemental weight percentage obtained from a Rabbit diesel tested within that study was 1.9 percent over the FTP using the National Average diesel fuel.

AMES TEST RESULTS - A matrix of 18 particulate extract samples was tested and consisted of one sample for each test cycle from both the Oldsmobile and Rabbit. An addition-

Table 11 - Trace Metal Emissions, mg/mi, Oldsmobile Diesel

EMISSIONS/TEST	FTP	FET	CUE	NYCC	SC	45-55
NA	0.2113	0.2291	0.0523	0.3219	0.1155	0.2593
MG	0.1238	0.5470	0.0520	0.2522	0.0040	0.1045
AL	0.0423	0.0179	0.0159	0.0225	0.0078	0.0146
SI	0.0338	0.0316	0.0246	0.0491	0.0318	0.0282
P	0.9411	0.9064	0.7238	1.8202	0.7094	1.0938
S	2.9565	3.5895	2.3212	4.1592	3.1590	3.2813
CL	0.0245	0.0243	0.02749	0.0485	0.0351	0.0157
CA	1.6567	1.5099	1.1842	3.1539	1.2001	1.9042
CR	0.2725	0.1912	0.1796	0.2248	0.0686	0.3644
MN	0.2571	0.1437	0.1274	0.3519	0.0809	0.3586
FE	0.2207	0.2528	0.1007	0.2960	0.2019	0.0754
CO	0.0621			0.0062	0.0219	0.0311
ZN	3.1121	3.2319	2.1517	4.3625	2.8716	3.8757
CD	0.0143	0.0195	0.0121	0.0174	0.0193	0.0224
SN	0.6254		0.0460	0.0638	0.0415	0.0925
SB	0.2319	0.2135	0.1645	0.4339	0.1617	0.2755
K	0.0091	0.0138	0.0052	0.0257	0.0144	0.0137
CU					0.0830	

Table 12 - Trace Metal Emissions, mg/mi, VW Rabbit Diesel

EMISSIONS/TEST	FTP	FET	CUE	NYCC	SC	45-55
NA	.3340	.1216	.1655	1.5481	.2723	.0590
MG	.1654	.6901	.0904	.4024	.1793	.0188
AL	.5306	.0039		.2087	.0118	.0028
S	4.1595	2.1492	2.3982	7.2862	3.9790	.8701
CA	3.1208	1.5705	1.1849	18.8184	3.059	.6830
P	1.2303	.9128	.4186	8.7967	1.7660	.4068
FE	.8747	.0423	.3555		.3178	
ZN	.4156	2.2444	2.5460	8.3516	4.4446	.9741
CD	.0067	.0050	.0181		.0330	.0047
SB	.4040	.1960	.1235	2.3254	.3865	.0952
BA	.0392		.0053	.1827	.0442	
PB	1.5789	1.1749	.4860		1.2587	.3285
CL		.0207	.0536			
CU			.0251		.0497	.0061
BR		.2370	.1465	2.1528	.1331	.0140
TI			.0063		.3757	.0667

al six FTP samples from the Rabbit were tested; of these, four reflected an injector malfunction (a faulty spray pattern existed on one injector.) Initial results were obtained only in strain TA 98 without microsomal activation. Experience to date with diesel samples has shown that tests using strain TA 98 without activation have produced higher revertant levels than tests with activation. By testing the matrix in a single experiment, data in the following areas was sought relative to mutagenicity:

1. Day to day variability of FTP test cycle.
2. Variations among cycles and comparison of cycles between the Oldsmobile and Rabbit.
3. Effects of injector malfunction.

Figure 8 shows the results obtained for a series of FTP's run on the Rabbit. During the first four test dates, the car had an injector malfunction. The last three test were run following injector tip replacement. Both sets of runs showed fair repeatability with an average relative standard deviation of 10.5 percent. However, injector malfunction resulted in a 73 percent increase in mutagenicity. Recent work by the Nissan Motor Company has also demonstrated that significant changes in the mutagenicity of particulate extracts can be attributed to injector malfunction (19).

Figures 9 and 10 are comparisons of the Oldsmobile and Rabbit for the six different test cycles studied. In Figure 9, the mutagenic activity is expressed in terms of revertants per microgram of extract and shows the Oldsmobile to be higher for the FTP, NYCC and SC, while the Rabbit is higher in the HWFET, CUE and 45 SS. However, when the mutagenic activity is normalized with respect to the extractable organics and particulate emissions, i.e., activity is expressed in revertants per mile, the Rabbit is higher for all test cycles except the NYCC as shown in Figure 10. However, the high activity calculated for the Oldsmobile in the NYCC is likely an atypical value since the particulate emissions for that individual test were more than double that normally observed.

Chemical characterization of the organic extracts is currently in progress. Initial efforts are being directed toward quantifying the nitro-aromatics, especially the nitropyrenes which have recently been reported to be mutagenic (20) and have also been identified in diesel extracts (21). The concentration of these compounds and their related mutagenic activity will then be correlated with the observed Ames test results.

CONCLUSIONS

1. Emissions of particulate matter and regulated gases measured from the Rabbit diesel when tested with

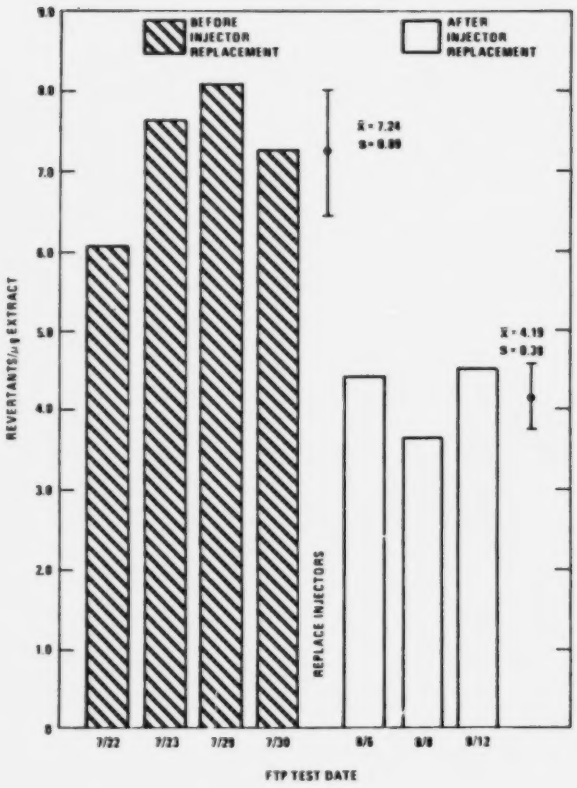

Fig. 8 - Comparison of extract mutagenicity for VW Rabbit diesel before and after injector replacement (Ames Test, TA 98-S9)

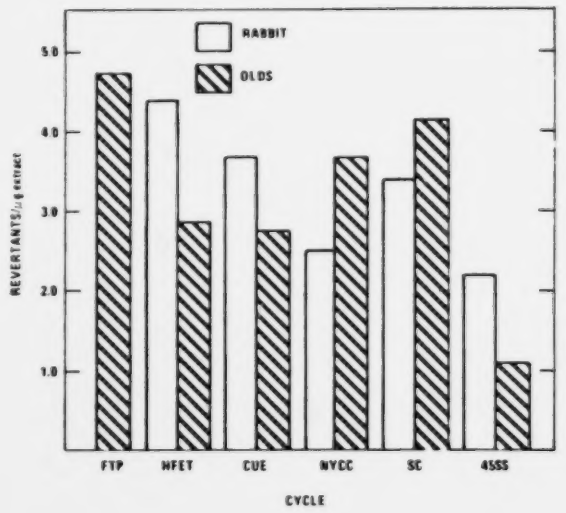

Fig. 9 - Comparison of extract mutagenicity for Oldsmobile diesel vs. VW Rabbit diesel (Ames Test, TA 98-S9)

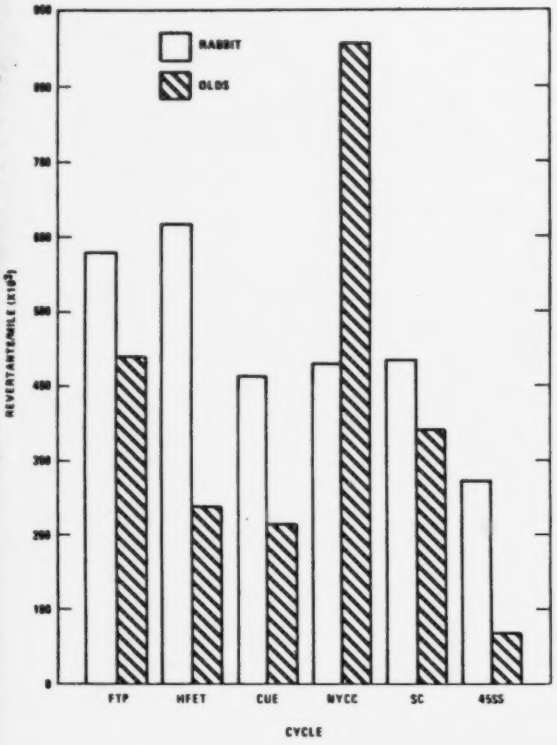

Fig. 10 - Comparison of mutagenicity expressed in revertants/mi, Oldsmobile diesel vs. VW Rabbit diesel (Ames Test, TA 98-S9)

one faulty injector tip were significantly higher than those measured after the tip was replaced.

2. The injector malfunction had a larger impact on mutagenic emissions than the cycle over which the vehicle was operated.
3. Differences in emissions and fuel economy for the FTP and FTP-U cycles were not detectable for the two diesel cars examined modally.
4. For the two vehicles examined, CO and HC g per mi emission rates were most sensitive and NOx emissions the least sensitive to changes in acceleration rate.
5. SOF extract quantities obtained using the Delta Filter Method agreed well with those determined using the direct weighing procedure.
6. Regulated gaseous emission rates obtained using the CVS system method agreed well with those obtained using the real-time method.
7. Trace metal emissions represented an insignificant portion of the total particulate mass.
8. Particulate sulfate emissions expressed as a percentage of the total particulate matter emitted were not significantly affected by the driving cycle.

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The content of this publication does not necessarily reflect the view or policies of the U.S. Environmental Protection Agency, nor does mention of trade names, commercial products, or organizations imply endorsement by the U.S. Government.

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